

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
25 October 2001 (25.10.2001)

PCT

(10) International Publication Number
WO 01/79397 A2

- (51) International Patent Classification⁷: **C10L**
- (21) International Application Number: **PCT/EP01/04177**
- (22) International Filing Date: **11 April 2001 (11.04.2001)**
- (25) Filing Language: **English**
- (26) Publication Language: **English**
- (30) Priority Data:
0009310.4 17 April 2000 (17.04.2000) **GB**
- (71) Applicant (*for all designated States except US*): **INFINEUM INTERNATIONAL LTD.** [GB/GB]; P.O. Box 1, Law Department, Milton Hill, Abingdon, Oxon, Oxfordshire OX13 6BB (GB).
- (72) Inventors; and
- (75) Inventors/Applicants (*for US only*): **JACKSON, Graham** [GB/GB]; 270A Kidmore Road, Caversham, Reading, Berkshire. Berkshire RG4 7NE (GB). **FAVA, Carlo** [IT/GB]; 7B Blandford Avenue, Oxford, Oxfordshire OX2 8EA (GB).
- (74) Agent: **HART, Richard, Joseph**; Infineum UK Limited, Law Department, PO Box 1, Milton Hill, Abingdon, Oxon, Oxfordshire OX13 6BB (GB).
- (81) Designated States (*national*): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CR, CU, CZ, DE, DK, DM, DZ, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW.
- (84) Designated States (*regional*): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).
- Published:**
— *without international search report and to be republished upon receipt of that report*
- For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.*



WO 01/79397 A2

(54) Title: **FUEL OIL COMPOSITIONS**

(57) Abstract: **Oils having improved lubricity and low temperature properties and additives for use therein.**

Fuel Oil Compositions

This invention relates to improved oil compositions and improved additive concentrates therefor, in particular to fuel oil compositions having improved lubricity properties and to additives enhancing a variety of fuel properties and providing operational advantages for fuel manufacturers and users.

Concern for the environment has resulted in moves to significantly reduce the noxious components in emissions when fuel oils are burnt, particularly in engines such as diesel engines. Attempts are being made, for example, to minimise sulphur dioxide emissions. As a consequence attempts are being made to minimise the sulphur content of fuel oils. Additional refining of fuel oils, necessary to achieve these low sulphur levels, often results in reductions in the level of polar components. In addition, refinery processes can reduce the level of polynuclear aromatic compounds present in such fuel oils.

Reducing the level of one or more of the sulphur, polynuclear aromatic or polar components of diesel fuel oil can reduce the ability of the oil to lubricate the injection system of the engine so that, for example, the fuel injection pump of the engine fails relatively early in the life of an engine. The problem of poor lubricity in diesel fuel oils is likely to be exacerbated by the future engine developments aimed at further reducing emissions, which will have more exacting lubricity requirements than present engines. Similarly, poor lubricity can lead to wear problems in other mechanical devices dependent for lubrication on the natural lubricity of fuel oil.

Further, many oil, and particularly fuel oil, compositions suffer from the problem of reduced flowability and/or filterability at low temperatures, due to the precipitation of the heavier alkanes (and particularly n-alkanes) inherent in such oils. This problem of alkane crystallisation at low temperatures is well known in the art. Additive solutions to this problem have been proposed for many years, in particular, copolymers of ethylene and vinyl esters such as vinyl acetate or vinyl propionate

have been successfully used in commercial applications and are well documented in the patent literature.

The problem of poor low temperature filterability has conventionally been measured by the Cold Filter Plugging Point ("CFPP") test, which determines the ease with which fuel moves under suction through a filter grade representative of field equipment.

In recent years, other fuel performance requirements have grown in importance. In particular, the degree of settling of precipitating n-alkane crystals has an important influence on the tendency of such crystals to interrupt fuel supply. Other additives, known as "Wax Anti-Settling Additives", and typically based on oil soluble polar nitrogen-containing compounds, have been developed to reduce the rate of settling of precipitating n-alkanes and so enhance this aspect of fuel low temperature behaviour. Such additives are typically used in conjunction with the conventional CFPP enhancing ethylene polymers.

Lubricity additives for fuel oils have been described in the art. WO 94/17160 describes an additive which comprises an ester of a carboxylic acid and an alcohol wherein the acid has from 2 to 50 carbon atoms and the alcohol has one or more carbon atoms. Glycerol monooleate is specifically disclosed as an example.

WO 98/16596 discloses certain esters of specific substituted aromatic carboxylic acids to show improved lubricity performance.

There, however, exists in the art a continual need for additives showing enhanced performance over existing materials, due not only to the development of engines with more exacting performance, but also to the general demand from consumers and fuel producers for higher quality fuels.

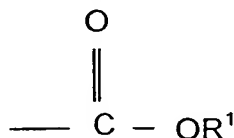
It has now been unexpectedly found that certain esters of aromatic carboxylic acids provide improved lubricity performance to fuel oil, particularly at lower treat-rates, when used in combination with at least one aromatic condensate or at least one

ethylene polymer or a mixture of both. Such additive combinations may show performance better than that predicted from their individual properties.

Further, the low temperature properties of a fuel oil can be maintained or even enhanced by addition thereto of certain esters of aromatic carboxylic acids without increasing the overall additive treat-rate.

In a first aspect, this invention provides a fuel oil composition comprising, or obtainable by admixing, a major amount of a fuel oil and minor amounts of,

- (I) one or more compounds having at least one aromatic ring system, wherein at least one ring system bears, as substituents,
 - (a) one or more hydroxyl groups or derivatives thereof or both; and
 - (b) one or more ester groups of the formula



where R^1 represents a hydrocarbyl group having at least one hydroxyl group or derivatives thereof or both;

- (II) one or more aromatic condensates other than those defined in (I) or one or more ethylene polymers or both; and
- (III) optionally, one or more oil-soluble polar nitrogen compounds.

In a second aspect, this invention provides an additive composition comprising, or obtainable by admixing, (I), (II) and optionally (III) as defined under the first aspect.

In a third aspect, this invention provides an additive concentrate comprising, or obtainable by admixing, either the additive composition of the second aspect or (I), (II) and optionally (III) as defined under the first aspect, and a compatible solvent therefor.

In a fourth aspect, this invention provides a fuel oil composition obtainable by admixing a fuel oil and either the additive composition of the second aspect or the additive concentrate of the third aspect.

- 5 In particular, the compounds defined under the first aspect of the invention provide, upon addition to low sulfur fuel oils an improvement in fuel lubricity which can exceed that obtainable from existing lubricity additives, especially mixtures of the individual esters disclosed in WO 94/17160.
- 10 Gasoline fuels are also subject to compositional constraints, including restrictions on the sulfur content, in an effort to reduce pollutants. The principle concern is the effect of sulfur on exhaust catalyst life and performance. The lubricity requirements of gasoline are somewhat lower than for diesel fuel since the majority of gasoline fuel injection systems inject fuel upstream of the inlet valves and thus operate at much
- 15 lower pressures than diesel pumps. However, as automobile manufacturers desire to have electrically powered fuel pumps within the fuel tanks, failure of these pumps can be expensive to repair. These problems are also likely to increase as injection systems become more sophisticated and gasoline fuels become more highly refined.
- 20 Additional pump wear concerns have arisen with the introduction of vehicles having gasoline direct injection engines since the fuel pumps for these vehicles operate at significantly higher pressures than traditional gasoline fuel pumps.

Another area subject to pump wear and failure is the use of submerged fuel pumps in

25 gasoline or diesel engine fuel storage tanks. It is important to reduce the wear of these submerged pumps due to the difficulty of getting to these pumps for repair and maintenance.

Many commercially available gasoline fuels contain gasoline detergents such as

30 polyisobutylene amine and polyether amine. These compounds are known to have a minor effect on the wear properties of these fuels. A growing number of commercially available gasoline fuels contain oxygenates, such as

methyltertiarybutylether (MTBE). These oxygenates are known to increase rates of wear of fuel pump components as they have very high friction coefficients.

Also there has been considerable effort in recent years to improve the fuel economy of motor vehicles. One approach to reducing fuel consumption has been development of additives which reduce engine friction in the combustion chamber of an internal combustion engines and thus reduce energy requirements.

In light of the desire for more highly refined fuels, lower sulfur content and oxygenation of the fuels and fuel oil compositions demonstrating improved fuel economy, there is a continuing need for lubricity improvers.

An advantage of the present invention is that the lubricity additive does not adversely impact upon activity of other additives, such as detergents. Indeed, the lubricity additive of the present invention has been found to minimise undesirable properties, such as inlet valve deposits, compared to other lubricity additives.

Accordingly, in a fifth aspect, this invention provides a fuel oil composition comprising, or obtainable by admixing, a major amount of hydrocarbons boiling in the gasoline range and minor amounts of (I) as defined in the first aspect, and optionally one or more gasoline co-additives selected from anti-knock agents, lead scavengers, detergents, dispersants, antioxidants, metal deactivators and carburetor or fuel injector detergents.

In a sixth aspect, this invention provides an additive composition comprising, or obtainable by admixing, (I) as defined in the first aspect and optionally one or more gasoline co-additives selected from anti-knock agents, lead scavengers, detergents, dispersants, antioxidants, metal deactivators and carburetor or fuel injector detergents.

In a seventh aspect, this invention provides a concentrate comprising, or obtainable by admixing, either the additive composition of the sixth aspect or (I) as defined in the

first aspect and one or more gasoline co-additives selected from anti-knock agents, lead scavengers, detergents, dispersants, antioxidants, metal deactivators and carburetor or fuel injector detergents, and a compatible solvent therefor.

- 5 In a eighth aspect, this invention provides the use of (I) as defined in the first aspect and optionally one or more gasoline co-additives selected from anti-knock agents, lead scavengers, detergents, dispersants, antioxidants, metal deactivators and carburetor or fuel injector detergents for improving the friction of a fuel composition comprising a major amount of hydrocarbons boiling in the gasoline range.

10

The aspects of the invention and other advantages of the invention will become apparent from the following description.

Fuel Oil Composition (First, Fourth and Fifth Aspects)

15 **The Compound(s) (I)**

The compound may comprise one or more aromatic ring systems. By 'aromatic ring system' in this specification is meant a planar cyclic moiety which may be an aromatic homocyclic, heterocyclic or fused polycyclic assembly or a system where two or more such cyclic assemblies are joined to one another and in which the cyclic
20 assemblies may be the same or different. It is preferred that the or each aromatic ring system is system based on heterocyclic or homocyclic 5-or 6- membered rings, more preferably 6-membered rings and most preferably benzene rings.

The ring atoms in the aromatic system are preferably carbon atoms but may for
25 example include one or more heteroatoms such as N, S, or O in the system in which case the compound is a heterocyclic compound.

It is preferred that at least one aromatic ring system of the compound contains one or more hydrocarbon groups as substituents, either bonded directly or indirectly to a ring
30 atom of the aromatic ring system, preferably bonded directly. Preferably, at least one of the hydrocarbon groups is capable of imparting fuel oil solubility to the compound.

Where the compound comprises only one aromatic ring system, it is preferred that one of each of the substituents (a) and (b) is present in such a compound. One, two or three hydrocarbon substituents may also be present, at least one of which is preferably capable of imparting fuel oil solubility to the compound.

5

Where the compound comprises two or more aromatic ring systems, it is preferred that at least one of the systems bears substituents (a) and (b). Preferably at least one ring system bears one of each substituent (a) and (b).

10 Particularly preferred are compounds wherein the or each aromatic ring system is a single, 6-membered ring, especially a benzene structure. Most preferably, the compound comprises a single benzene ring and having one of each of the (a) and (b) substituents, wherein substituent (a) is a hydroxyl group.

15 By the term hydrocarbon as used in this specification in relation to the substituent on the ring system is meant an organic moiety which is composed of hydrogen and carbon, which is bonded to the rest of the molecule by a carbon atom or atoms which unless the context states otherwise, may be aliphatic, including alicyclic, aromatic or a combination thereof. It may be substituted or unsubstituted alkyl, aryl or alkaryl and
20 may optionally contain unsaturation. The organic moiety may also contain heteroatoms, such as oxygen, nitrogen or sulfur, provided that such heteroatoms are insufficient to alter the essentially hydrocarbon character of the substituent.

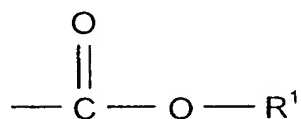
It is preferred that the hydrocarbon substituent is aliphatic, for example alkyl or
25 alkenyl, which may be branched or preferably straight-chain. Straight-chain alkyl is preferred.

It is preferable that at least one hydrocarbon substituent be a hydrocarbon group of sufficient oleophilic character to impart fuel oil solubility to the compound. In this
30 respect, it is preferred that at least one hydrocarbon substituent contains at least 8 carbon atoms, and preferably 10 to 200 carbon atoms. A substituent having 12 to 54, for example 14 to 36 carbon atoms is particularly preferred. Most preferred are

alkyl or alkenyl groups containing 12 to 54 carbon atoms, especially straight chain alkyl groups. The groups having 14 to 20 carbon atoms are most advantageous.

Substituent (a) is a hydroxyl group or derivative thereof. When a hydroxyl group, the compound may show particularly good performance as an oxidation inhibitor.

Substituent (b) is an ester group, wherein the carbonyl carbon of the ester is bonded indirectly, or preferably directly, to a ring atom of the aromatic ring system and more preferably to a ring carbon. The ester group is of the formula:



wherein the group --- OR^1 is derivable from the corresponding alcohol HOR^1 , wherein R^1 represents a hydrocarbyl group having at least one hydroxyl group substituent or a derivative thereof or both. Preferably the hydrocarbyl group substituent has at least one hydroxyl group.

By the term hydrocarbyl in this specification is meant an organic moiety which is composed of hydrogen and carbon and which is bonded to the rest of the molecule by a carbon atom or atoms and which includes hydrocarbon groups as hereinbefore defined in relation to substituents on the ring system, as well as predominantly-hydrocarbon groups containing heteroatoms such as O, N or S provided that such heteroatoms are insufficient to alter the essentially hydrocarbon nature of the group.

Examples of R^1 include 2-hydroxyethyl, 3-hydroxypropyl, 4-hydroxybutyl, ethoxyethyl, and propoxypropyl.

Particularly good results have been achieved when the alcohol HOR^1 is a polyhydroxy alcohol, each hydroxyl group being bonded to a different carbon atom of the alcohol.

The most favoured alcohols are polyhydroxyalcohols giving rise in the compound to ester groups comprising hydroxy - substituted alkyl substituents. Suitable polyhydroxy alcohols are aliphatic, saturated or unsaturated, straight chain or branched alcohols having 2 to 10, preferably 2 to 6, more preferably 2 to 4, hydroxyl groups, and having 2 to 90, preferably 2 to 30, more preferably 2 to 12, most preferably 2 to 5, carbon atoms in the molecule. As examples, the polyhydroxy alcohol may be a glycol or diol, or a trihydroxy alcohol. Ethylene glycol and glycerol are most highly preferred.

In the compound, the substituents (a) and (b) are preferably positioned vicinally on the aromatic ring system from which they depend. Where the system is polycyclic they are preferably positioned vicinally on the same ring of the polycyclic system, for example in an ortho position to each other, although they may be positioned on different rings. The or each hydrocarbon on the ring system substituent may be positioned vicinally to any of the substituents (a) or (b), or in a position further removed in the ring system.

The compound may also be of oligomeric structure, such as a series of aromatic ring systems connected via esterification with polyhydric alcohols, or via alkylene bridges produced, for example, by the phenol-formaldehyde type condensation reaction of several aromatic ring systems with an aldehyde. Particularly useful are methylene - bridged compounds wherein each aromatic ring system is preferably a homocyclic, six-membered ring and wherein, more preferably, each ring carries at least one of each of the substituents (a) and (b).

Preferably, the compound is fuel oil-soluble.

The compound may be prepared by conventional means. Thus, for example, the compound may be prepared by esterification of a precursor compound having the requisite aromatic ring system or systems bearing hydrocarbon substituent and/or substituent (a) and one or more carboxylic acid substituents, or acylating derivatives

thereof, capable of esterification with compounds having at least one hydroxyl group to form substituent (b).

Preferably, the compound is the ethylene glycol or ethylene oxide or glycerol ester of salicylic acid or substituted salicylic acid.

The Aromatic Condensate(s) (II)

The aromatic condensate is obtainable by the condensation reaction between:

- (i) at least one aldehyde or ketone or reactive equivalent thereof, and
- (ii) at least one compound comprising one or more aromatic moieties bearing at least one substituent of the formula $-XR^{10}$ and at least one further substituent $-R^{11}$, wherein:
 - X represents oxygen or sulphur,
 - R^{10} represents hydrogen or moiety bearing at least one hydrocarbyl group, and
 - R^{11} represents a hydrocarbyl group and contains less than 18 carbon atoms when a linear group.

Reactant (i) comprises one or more aldehydes or ketones or reactive equivalents thereof. By "reactive equivalent" is meant a material which generates an aldehyde under the conditions of the condensation reaction or a material which undergoes the required condensation reaction to produce moieties equivalent to those produced by an aldehyde. Typical reactive equivalents include oligomers or polymers of the aldehyde, acetals, or aldehyde solutions.

Particularly preferred reactants (i) are formaldehyde, acetaldehyde, the butyraldehydes and substituted analogues or reactive equivalents thereof. Formaldehyde and glyoxylic acid (or pyruvic acid) are particularly preferred.

5 Reactant (ii) preferably comprises one or more compounds wherein each aromatic moiety bears one substituent of the formula $-XR^{10}$. More preferably, (ii) bears one substituent of the formula R^{11} and most preferably, also one substituent of the formula $-XR^{10}$. X is preferably oxygen.

10 Most preferably, the aromatic moiety is a benzene or substituted benzene nucleus.

In every aspect of the invention, a preferred Reactant (ii) comprises a benzene nucleus bearing one substituent of formula $-XR^{10}$ and one substituent of formula R^{11} .

15 R^{10} may represent a moiety bearing a hydrocarbyl group, where hydrocarbyl is as defined above in relation to the compound (I). Preferably, the hydrocarbyl group in R^{10} is an aliphatic group, such as alkenyl or alkyl group, which may be branched or preferably straight chain. The hydrocarbyl group in R^{10} may be bonded directly to the oxygen or sulphur atom (represented by X in the formula $-XR^{10}$) or may be bonded
20 indirectly by means of a functional group, for example on ester, ether, peroxide, anhydride or polysulphide linkage.

Preferably, where R^{10} is hydrocarbyl, the hydrocarbyl group in R^{10} contains 8-40 carbon atoms, more preferably 12-24 carbon atoms, such as 12-18 carbon atoms.

25 Most preferably, R^{10} is hydrogen.

R^{11} may independently represent those hydrocarbyl groups contemplated as forming part of the moiety R^{10} , although typically R^{10} and R^{11} (where both are present) will on any one aromatic moiety, will be different from each other, and may be the same or
30 different on different aromatic moieties.

Preferably, R^{11} is an alkenyl or, more preferably, alkyl group, most preferably containing less than 18 carbon atoms. More preferably, R^{11} is a branched chain group, preferably an alkyl group. Most preferred embodiments of R^{11} include branched chain alkyl groups containing less than 16 carbon atoms, for example 4 to 16 carbon atoms, such as groups containing 8, 9, 12 or 15 carbon atoms. Groups containing 9 carbon atoms are most preferred. Minor amounts of short chain alkyl groups (e.g. 4 carbons or less) may be present.

Preferably, the aromatic condensate is a condensate of formaldehyde and phenol.

Preferably, the aromatic condensate is formed from a reactant (ii) which comprises at least one aliphatic hydrocarbyl-substituted phenol, such as branched chain C_9 or C_{15} alkyl phenol, for example nonyl phenol.

The aromatic condensate may be combined with at least one amine bearing at least one hydrocarbyl substituent. Such combination may be purely by admixture, but is preferably by physical or chemical association or complexation. More preferably, the aromatic condensate is reacted with at least one amine, more preferably to form the amine salt derivative thereof.

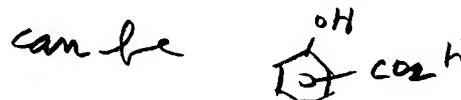
In a preferred embodiment, the aromatic condensate may be formed by the reaction of (i), (ii) and at least one further reactant (iii), wherein reactant (iii) comprises at least one compound comprising one or more aromatic moieties bearing at least one substituent of the formula $-XR^{10}$ and at least one further substituent $-R^{12}$ wherein:

- X represents oxygen or sulphur,

- R^{10} represents hydrogen or a moiety bearing at least one hydrocarbyl group; and

- R^{12} represents a $COOH$ or SO_3H group or derivative thereof.

es formaldehyde → *can be $RPhOH$ where R is $<C_{18}$ when linear*



Preferably, reactant (iii) is salicylic acid or a substituted derivative thereof, or p-hydroxy-benzoic acid or a substituted derivative thereof.

Preferably the product obtainable from reaction of (i), (ii) and (iii) are combined with at least one amine, as described above. In such products, the amine is preferably reacted with the substituents of the formula $-R^3$, e.g. the $-\text{COOH}$ or $-\text{SO}_3\text{H}$ groups, so as to form the amine salt derivatives thereof; although salt formation may additionally occur via any $-\text{OH}$ substituents.

Preferred as the aromatic condensate are embodiments obtainable from at least one alkyl phenol (i) wherein the alkyl substituent contains no more than 15 carbon atoms, formaldehyde or a reactive equivalent thereof, and optionally (iii) salicylic acid, and wherein the amine is an alkyl or dialkyl amine, preferably as described above and more preferably selected from dihydrogenated tallowamine, dicocoamine, and mixtures thereof.

Preferably, the aromatic condensate is fuel-soluble.

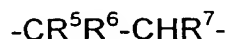
Aromatic condensates disclosed in EP-A-0857776, PCT/EP/99/03306 and PCT/EP/99/03308 are within the scope of the present invention.

The Ethylene Polymer(s) (II)

Each polymer may be a homopolymer or a copolymer of ethylene with another unsaturated monomer. Suitable co-monomers include hydrocarbon monomers such as propylene, n- and i- butylene and the various α -olefins known in the art, such as decene-1, dodecene-1, tetradecene-1, hexadecene-1 and octadecene-1.

Preferred co-monomers are unsaturated ester or ether monomers, with ester monomers being more preferred. Thus, an ethylene unsaturated ester copolymer is preferred.

Preferred ethylene unsaturated ester copolymers have, in addition to units derived from ethylene, units of the formula:



wherein R^5 represents hydrogen or methyl, R^6 represents $-\text{COOR}^8$, wherein R^8 represents an alkyl group having from 1-12, preferably 1-9 carbon atoms, which is a straight chain, or, if it contains 3 or more carbon atoms, branched, or R^6 represents OOCR^9 , wherein R^9 represents R^8 or H, and R^7 represents H or COOR^8 .

These may comprise a copolymer of ethylene with an ethylenically unsaturated ester, or derivatives thereof. An example is a copolymer of ethylene with an ester of a saturated alcohol and an unsaturated carboxylic acid, but preferably the ester is one of an unsaturated alcohol with a saturated carboxylic acid. An ethylene vinyl ester copolymer is advantageous; an ethylene vinyl acetate, ethylene vinyl propionate, ethylene vinyl hexanoate, ethylene vinyl 2-ethylhexanoate, ethylene vinyl octanoate or ethylene vinyl versatate copolymer is preferred. Preferably, the copolymer contains from 5 to 40 wt% of the vinyl ester, more preferably from 10 to 35 wt% vinyl ester. A mixture of two copolymers, for example as described in US Patent No. 3,961,916, may be used. The number average molecular weight of the copolymer, as measured by vapour phase osmometry, is advantageously 1,000 to 10,000, preferably 1,000 to 5,000. If desired, the copolymer may contain units derived from additional comonomers, e.g. a terpolymer, tetrapolymer or a higher polymer, for example where the additional comonomer is isobutylene or disobutylene, or a further unsaturated ester.

Within the meaning of this specification, "copolymer" refers to a polymer obtained from two or more different co-monomers.

Most preferably, the ethylene polymer comprises an ethylene vinyl acetate or ethylene vinyl propionate copolymer, or a mixture thereof, or a terpolymer of ethylene and two vinyl esters, each giving rise to polymer units corresponding to the above

formula. Particularly preferred are terpolymers of ethylene, vinyl acetate and a third unsaturated ester monomer, for example, selected from vinyl propionate, vinyl 2-ethyl hexanoate, or vinyl versatate.

- 5 Preferably, the ethylene polymer is fuel-soluble.

The Oil Soluble Polar Nitrogen Compound(s) (III)

Such compounds carry one or more, preferably two or more, substituents of the formula $>NR^{13}$, where R^{13} represents a hydrocarbyl group containing 8-40 carbon
10 atoms, which substituent or one or more of which substituents may be in the form of a cation derived therefrom. R^{13} preferably represents an aliphatic hydrocarbyl group containing 12-24 carbon atoms. The oil soluble polar nitrogen compound is capable of acting as a wax crystal growth inhibitor in fuels.

- 15 Preferably, the hydrocarbyl group is linear or slightly linear, i.e. it may have one short length (1-4 carbon atoms) hydrocarbyl branch. When the substituent is amino, it may carry more than one said hydrocarbyl group, which may be the same or different.

The polar nitrogen compound may comprise one or more amino or imino
20 substituents. More especially, the or each amino or imino substituent is bonded to a moiety via an intermediate linking group such as $-CO-$, $-CO_2(-)$, $-SO_3(-)$ or hydrocarbylene. Where the linking group is anionic, the substituent is part of a cationic group, as in an amine salt group.

- 25 When the polar nitrogen compound carries more than one amino or imino substituent, the linking groups for each substituent may be the same or different.

Suitable amino substituents are long chain C_{12} - C_{40} , preferably C_{12} - C_{24} , alkyl primary, secondary, tertiary or quaternary amino substituents.

Preferably, the amino substituent is a dialkylamino substituent, which, as indicated above, may be in the form of an amine salt thereof; tertiary and quaternary amines can form only amine salts. Said alkyl groups may be the same or different.

5 Preferred amino substituents are the secondary hydrogenated tallow amino substituent, the alkyl groups of which are derived from hydrogenated tallow fat and are typically composed of approximately 4% C₁₄, 31% C₁₆ and 59% C₁₈ n-alkyl groups by weight, and the dicocoamino substituent, composed predominantly of C₁₂ and C₁₄ n-alkyl groups.

10 Suitable imino substituents are long chain C₁₂-C₄₀, preferably C₁₂-C₂₄, alkyl substituents.

15 Said polar nitrogen compound is preferably monomeric (cyclic or non-cyclic) or aliphatic polymeric, but is preferably monomeric. When non-cyclic, it may be obtained from a cyclic precursor such as an anhydride or a spirobis lactone.

20 The cyclic ring system of the compound may include homocyclic, heterocyclic, or fused polycyclic assemblies in which the cyclic assemblies may be the same or different. Preferably, the or each cyclic assembly is aromatic, more preferably a benzene ring. Most preferably, the cyclic ring system is a single benzene ring when it is preferred that the substituents are in the ortho or meta positions, which benzene ring may be optionally further substituted.

25 The ring atoms in the cyclic assembly or assemblies are preferably carbon atoms but may for example include one or more ring N, S or O atom, in which case or cases the compound is a heterocyclic compound.

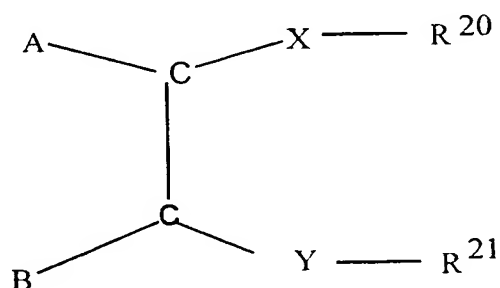
Examples of polar nitrogen compounds are described below:

- 30
- (i) Amine salts and/or amides of mono- or poly- carboxylic acids or reactive equivalents thereof (e.g. anhydrides), e.g. having 1-4 carboxylic acid groups.

Each may be made, for example, by reacting at least one molar proportion of a hydrocarbyl substituted amine with a molar proportion of the acid or its anhydride.

5 When an amide is formed, the linking group is $-\text{CO}-$; when an amine salt is formed, the linking group is $-\text{CO}_2(-)$.

(ii) Polar nitrogen compounds of the general formula:



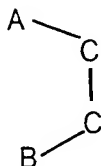
10 in which $-\text{Y}-\text{R}^{21}$ is $\text{SO}_3^{(-)(+)}\text{NR}_3\text{R}^{21}$, $-\text{SO}_3^{(-)(+)}\text{HNR}^{22}_2\text{R}^{21}$, $-\text{SO}_3^{(-)(+)}\text{H}_2\text{NR}^{22}\text{R}^{21}$, $-\text{SO}_3^{(-)(+)}\text{H}_3\text{NR}^{21}$, $-\text{SO}_2\text{NR}^{22}\text{R}^{21}$ or $-\text{SO}_3\text{R}^{21}$; and $-\text{X}-\text{R}^{20}$ is $-\text{Y}-\text{R}^{21}$ or $-\text{CONR}^{22}\text{R}^{20}$, $-\text{CO}_2^{(-)(+)}\text{NR}^{22}_3\text{R}^{20}$, $-\text{CO}_2^{(-)(+)}\text{HNR}^{22}_2\text{R}^{20}$, $-\text{R}^{23}-\text{COOR}$, $-\text{NR}^{22}\text{COR}^{20}$, $-\text{R}^{23}\text{OR}^{20}$, $-\text{R}^{23}\text{OCOR}^{20}$, $-\text{R}^{23}$, $-\text{R}^{20}$, $-\text{N}(\text{COR}^{22})\text{R}^{20}$ or $\text{Z}^{(-)(+)}\text{NR}^{22}_3\text{R}^{20}$; $-\text{Z}^{(-)}$ is $\text{SO}_3^{(-)}$ or $-\text{CO}_2^{(-)}$;

15

R^{20} and R^{21} are alkyl, alkoxyalkyl or polyalkoxyalkyl containing at least 10 carbon atoms in the main chain.

R^{22} is hydrocarbyl and each R^{22} may be the same or different and R^{23} is absent or is

20 C_1 to C_5 alkylene and in:



the Carbon-Carbon (C-C) bond is either:

(a) Ethylenically unsaturated when A and B may be alkyl, alkenyl or substituted hydrocarbyl groups or,

(b) Part of a cyclic structure which may be aromatic, polynuclear aromatic or cyclo-aliphatic,

(iii) Amines or diamine salts of:

(a) A sulphosuccinic acid,

(b) An ester or diester of a sulphosuccinic acid,

(c) An amide or a diamide of a sulphosuccinic acid, or

(d) An ester amide of a sulphosuccinic acid.

(iv) Chemical compounds comprising or including a cyclic ring system, the compound carrying at least two substituents of the general formula (I) below on the ring system:



where A is an aliphatic hydrocarbyl group that is optionally interrupted by one or more hetero atoms and that is straight chain or branched, and R^{25} and R^{26} are the same or different and each is independently a hydrocarbyl group containing 9-40 carbon atoms optionally interrupted by one or more hetero atoms, the substituents being the same or different and the compound optionally being in the form of a salt thereof.

(v) A condensate of long chain primary or secondary amine with an aliphatic carboxylic acid-containing polymer, such as a polymer of maleic anhydride and one

or more unsaturated monomers, for example ethylene or another α olefin such as C₆-C₃₀ α olefin.

Preferred polar nitrogen compounds are those wax anti-settling additives comprising the amides and/or amine salts, or mixtures thereof, of aromatic or aliphatic polycarboxylic acid (or reactive equivalents thereof) and alkyl or dialkyl amines, such as those formed from the following:

- (i) Benzene dicarboxylic acids (or anhydrides thereof), such as phthalic anhydride.
- (ii) Alkylene di- or polyamine tetraacetic or tetra propionic acids, such as EDTA (Ethylene Diamine Tetraacetic Acid), and
- (iii) Alkyl or alkenyl substituted succinic acids.

The preferred amines include dialkyl amines having 10-30, preferably 12-20 carbon atoms in each alkyl chain, for example dihydrogenated tallow amine or dicocamine, or mixtures thereof.

Compounds resulting from the reaction of phthalic anhydride and dialkyl amines, such as those specified above, are most preferred.

Therefore, the nitrogen compound is preferably an amine salt and/amide formed by reacting at least one molar proportion of a hydrocarbyl-substituted amine and a molar proportion of a hydrocarbyl acid having from 1 to 4 carboxylic acid groups or its anhydride, such as an amide – amine salt formed by reacting 1 molar portion of phthalic anhydride with 2 molar proportions of dihydrogenated tallow amine.

Preferably, the nitrogen compound is fuel-soluble.

The Fuel Oil

The fuel oil, with respect to the first or fourth aspect, may be a hydrocarbon fuel such as a petroleum-based fuel oil for example kerosene or distillate fuel oil, suitably a middle distillate fuel oil, i.e. a fuel oil obtained in refining crude oil as the fraction

5 between the lighter kerosene and jet fuels fraction and the heavier fuel oil fraction. Such distillate fuel oils generally boil within the range of about 100°C to about 500°C, e.g. 150° to about 400°C, for example, those having a relatively high Final Boiling Point of above 360°C (by ASTM-D86). The fuel oil can comprise atmospheric distillate or vacuum distillate, or cracked gas oil or a blend in any proportion of
10 straight run and thermally and/or catalytically cracked distillates. The most common petroleum distillate fuels are kerosene, jet fuels, diesel fuels, heating oils and heavy fuel oils, diesel fuels and heating oils being preferred. The diesel fuel or heating oil may be a straight atmospheric distillate, or may contain minor amounts, e.g. up to 35 wt %, of vacuum gas oil or cracked gas oils or both.

15 Also, the fuel oil may be of animal or vegetable oil origin (i.e. a 'biofuel'), or a mineral oil as described above in combination with one or more biofuels. Biofuels, being fuels from animal or vegetable sources, are obtained from a renewable source. Within this specification, the term "biofuel" refers to a vegetable or animal oil or both
20 or a derivative thereof. Certain derivatives of vegetable oil, for example of rapeseed oil, e.g. those obtained by saponification and re-esterification with a monohydric alcohol, may be used as a substitute for diesel fuel.

The fuel oil composition has a sulphur concentration of 0.2% by mass or less based
25 on the mass of the fuel oil composition, and preferably 0.05% or less, more preferably 0.03% or less, such as 0.01 % or less, most preferably 0.005% or less and especially 0.001% or less. Low sulfur fuels, for example having less than 0.2 % by mass of sulfur based on the mass of fuel oil, may be made by means and methods known in the fuel-producing art, such as solvent extraction, hydrodesulphurisation
30 and sulphuric acid treatment.

Preferred fuel oils have a cetane number of at least 50. The fuel oil may have a cetane number of at least 50 prior to the addition of any cetane improver or the cetane number of the fuel may be raised to at least 50 by the addition of a cetane improver. More preferably, the cetane number of the fuel oil is at least 52.

5

Preferably, the fuel oil is a middle distillate fuel oil, more preferably a diesel fuel oil.

The fuel oil, with respect to the fifth aspect, will be a fuel boiling in the gasoline boiling range, and it may consist substantially of hydrocarbons or it may contain blending components. Alternatively, e.g. in countries such as Brazil, the fuel may consist substantially of ethanol.

10

Suitable liquid hydrocarbon fuels of the gasoline boiling range are mixtures of hydrocarbon boiling in the temperature range from about 25°C to about 232°C, and comprise mixtures of saturated hydrocarbons, olefinic hydrocarbons and aromatic hydrocarbons. Preferred are gasoline mixtures having a saturated hydrocarbon content ranging from about 40% to about 80% by volume, an olefinic hydrocarbon content from 0% to about 30% by volume and an aromatic hydrocarbon content from about 10% to about 60% by volume. The base fuel is derived from straight run gasoline, polymer gasoline, natural gasoline, dimer and trimerized olefins, synthetically produced aromatic hydrocarbon mixtures, from thermally or catalytically reformed hydrocarbons, or from catalytically cracked or thermally cracked petroleum stocks, and mixtures of these. The hydrocarbon composition and octane level of the base fuel are not critical. The octane level, $(R+M)/2$, will generally be above about 85 (where R is Research Octane Number and M is Motor Octane Number).

15

20

25

Any conventional base gasoline can be employed in the practice of the present invention. For example, hydrocarbons in the gasoline can be replaced by up to a substantial amount of conventional alcohols or ethers, conventionally known for use in fuels. The base gasolines are desirably substantially free of water since water could impede a smooth combustion.

30

Normally, the gasolines to which the invention is applied may be leaded or unleaded, although are preferably substantially lead-free, and may contain minor amounts of one or more blending agents such as methanol, ethanol, tertiary butanol, ethyl tertiary butyl ether, methyl tertiary butyl ether, and the like, at from about 0.1% by volume to about 25% by volume of the base fuel, although larger amounts (e.g. up to 40%v) may be utilised.

The fuel oil composition, with respect to the first or fourth aspect, is preferably obtained by admixing a fuel oil and additives (I), (II) and optionally (III), or the additive composition or additive concentrate of the second or third aspect respectively of the present invention.

The fuel oil composition, with respect to the fifth aspect, is preferably obtained by admixing a fuel oil and additives (I), optionally one or more gasoline co-additives, or the additive composition or additive concentrate of the sixth or seventh aspect respectively of the invention.

The Additive Composition (Second and Sixth Aspects)

The additive composition is preferably obtained by admixing the additives as defined under either the first or fifth aspect.

The manufacture of the additive composition may be by methods known in the art. The additives, for example (I), (II) and optionally (III), may be blended, for example mixed, simultaneously or sequentially at ambient or elevated temperature. The additive composition may further comprise other co-additives (see below).

The Additive Concentrate (Third and Seventh Aspects)

The additive concentrate is preferably obtained by admixing, either the additive composition of the second or sixth aspect or the additives as defined under the first or fifth aspect, and a compatible solvent therefor.

Concentrates comprising the additives, for example as the additive composition, in admixture with a carrier liquid (e.g. as a solution or a dispersion) are convenient as a

means for incorporating the additives into bulk oil such as distillate fuel, which incorporation may be done by methods known in the art.

5 The additives of the invention may be incorporated into bulk oil by other methods such as those known in the art. If co-additives are required, they may be incorporated into the bulk oil at the same time as the additives of the invention or at a different time.

10 In this specification, the expression "comprising" refers both to compositions in which the additives, for example (I), (II) and optionally (III), exist discretely in their individual forms, and also to compositions in which, after admixing, interaction between one or more of the additives (including, where present, further optional additive components), such as complexation or other *in-situ* physical or chemical association leads to a loss of the discrete identity of the individual additives, but without
15 detracting significantly from the performance of the additives. Similarly, any of the compositions of the present invention may be obtained by the admixture of precursors to additives, for example (I), (II) and (III), and subsequent reaction to form the desired additives *in-situ* in the composition.

20 The terms "fuel- or oil-soluble" or cognate terms, used herein do not necessarily indicate that the compounds or additives are soluble, dissolvable, miscible, or are capable of being suspended in the fuel oil in all proportions. These do mean, however, that they are, for instance, soluble or stably dispersible in fuel oil to an extent sufficient to exert their intended effect in the environment in which the fuel is
25 employed. Moreover, the additional incorporation of other additives may also permit incorporation of higher levels of a particular additive, if desired.

Preferably, any one of the first to fourth aspects of the present invention (*i.e.* fuel oil composition, or additive composition, or additive concentrate) comprises (I), (II) and
30 (III); more preferably any one of the first to fourth aspects of the present invention comprises one or more compounds (I), one or more aromatic condensates, one or more ethylene polymers, and one or more oil-soluble polar nitrogen compounds (III).

Preferably, any one of the fifth to eighth aspects of the invention comprises additive (I) and at least one gasoline co-additive.

5 Co-additives

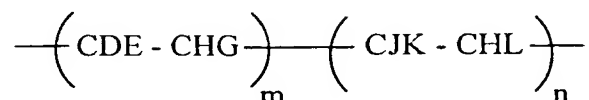
The fuel oil composition, additive composition, or additive concentrate of the first to fourth aspects may additionally comprise one or more co-additives useful in fuel oil compositions. Such co-additives include other cold flow improving additives, such as
10 one or more additives selected from the following classes:

- (i) comb polymers
- (ii) linear ester, ether, ester/ethers and mixtures thereof;
- (iii) non-ethylene hydrocarbon polymers, and
- 15 (iv) hydrocarbylated aromatic compounds.

(i) Generally, comb polymers consist of molecules in which long chain branches such as hydrocarbyl branches, optionally interrupted with one or more oxygen atoms and/or carbonyl groups, having from 12 to 30 such as 14 to 20, carbon atoms, are
20 pendant from a polymer backbone, said branches being bonded directly or indirectly to the backbone. Examples of indirect bonding include bonding via interposed atoms or groups, which bonding can include covalent and/or electrovalent bonding such as in a salt. Generally, comb polymers are distinguished by having a minimum molar proportion of units containing such long chain branches.

25 Advantageously, the comb polymer is a homopolymer having, or a copolymer at least 25 and preferably at least 40, more preferably at least 50, molar per cent of the units of which have, side chains containing at least 12 atoms, selected from for example carbon, nitrogen and oxygen, in a linear chain or a chain containing a small amount
30 of branching such as a single methyl branch.

As examples of preferred comb polymers there may be mentioned those containing units of the general formula



where D represents R^{30} , COOR^{30} , OCOR^{30} , $\text{R}^{31}\text{COOR}^{30}$ or OR^{30} ;
 E represents H, D or R^{31} ;
 G represents H or D;
 J represents H, R^{31} , $\text{R}^{31}\text{COOR}^{30}$, or a substituted or unsubstituted
 aryl or heterocyclic group;
 K represents H, COOR^{31} , OCOR^{31} , OR^{31} or COOH ;
 L represents H, R^{31} , COOR^{31} , OCOR^{31} or substituted or
 unsubstituted aryl;
 R^{30} representing a hydrocarbyl group having 12 or more carbon
 atoms, and
 R^{31} representing a hydrocarbyl group being divalent in the
 $\text{R}^{31}\text{COOR}^{30}$ group and otherwise being monovalent,

and m and n represent mole ratios, their sum being 1 and m being finite and being up
 to and including 1 and n being from zero to less than 1, preferably m being within the
 range of from 1.0 to 0.4, n being in the range of from 0 to 0.6. R^{30} advantageously
 represents a hydrocarbyl group with from 12 to 30 carbon atoms, preferably 12 to 24,
 more preferably 12 to 18. Preferably, R^{30} is a linear or slightly branched alkyl group
 and R^{31} advantageously represents a hydrocarbyl group with from 1 to 30 carbon
 atoms when monovalent, preferably with 6 or greater, more preferably 10 or greater,
 preferably up to 24, more preferably up to 18 carbon atoms. Preferably, R^{31} , when
 monovalent, is a linear or slightly branched alkyl group. When R^{31} is divalent, it is
 preferably a methylene or ethylene group. By "slightly branched" is meant having a
 single methyl branch.

The comb polymers may, for example, be copolymers of maleic anhydride or fumaric acid and another ethylenically unsaturated monomer, e.g. an α -olefin or an unsaturated ester, for example, vinyl acetate as described in EP-A-214,786. It is preferred but not essential that equimolar amounts of the comonomers be used although molar proportions in the range of 2 to 1 and 1 to 2 are suitable. Examples of olefins that may be copolymerized with e.g. maleic anhydride, include 1-dodecene, 1-tetradecene, 1-hexadecene, 1-octadecene, and styrene. Other examples of comb polymer include methacrylates and acrylates.

Other suitable comb polymers are the polymers and copolymers of α -olefins and esterified copolymers of styrene and maleic anhydride, and esterified copolymers of styrene and fumaric acid as described in EP-A-282,342.

Other examples of comb polymers are hydrocarbon polymers such as copolymers of ethylene and at least one α -olefin, preferably the α -olefin having at most 20 carbon atoms, examples being n-dodecene-1, n-tetradecene-1 and n-hexadecene-1 (for example, as described in WO9319106).

(ii) Such compounds comprise an ester, ether, ester/ether compound or mixtures thereof in which at least one substantially linear alkyl group having 10 to 30 carbon atoms is connected via an optional linking group that may be branched to a non-polymeric residue, such as an organic residue, to provide at least one linear chain of atoms that includes the carbon atoms of said alkyl groups and one or more non-terminal oxygen, sulphur and/or nitrogen atoms. The linking group may be polymeric.

By "substantially linear" is meant that the alkyl group is preferably straight chain, but that straight chain alkyl groups having a small degree of branching such as in the form of a single methyl group branch may be used.

The preferred esters, ethers or ester/ethers which may be used may comprise compounds in which one or more groups (such as 2, 3 or 4 groups) of formula $-OR^{25}$ are bonded to a residue E, where E may for example represent A (alkylene)_q, where

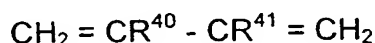
A represents carbon or nitrogen or is absent, q represents an integer from 1 to 4, and the alkylene group has from one to four carbon atoms, A (alkylene)_q for example being N(CH₂CH₂)₃; C(CH₂)₄; or (CH₂)₂; and R²⁵ may independently be

- (a) n-alkyl-
- (b) n-alkyl-CO-
- (c) n-alkyl-OCO-(CH₂)_n-
- (d) n-alkyl-OCO-(CH₂)_nCO-

n being, for example, 1 to 34, the alkyl group being linear and containing from 10 to 30 carbon atoms. For example, they may be represented by the formula R²³OBOR²⁴, R²³ and R²⁴ each being defined as for R²⁵ above, and B representing the polyalkylene segment of the glycol in which the alkylene group has from 1 to 4 carbon atoms, for example, polyoxymethylene, polyoxyethylene or polyoxytrimethylene moiety which is substantially linear; some degree of branching with lower alkyl side chains (such as in polyoxypropylene glycol) may be tolerated but it is preferred that the glycol should be substantially linear.

(iii) The non-ethylene hydrocarbon polymer may be an oil-soluble hydrogenated block diene polymer, comprising at least one crystallizable block, obtainable by end-to-end polymerisation of a linear diene, and at least one non-crystallizable block, the non-crystallizable block being obtainable by 1,2-configuration polymerisation of a linear diene, by polymerisation of a branched diene, or by a mixture of such polymerisations.

Advantageously, the block copolymer before hydrogenation comprises units derived from butadiene only, or from butadiene and at least one comonomer of the formula



wherein R⁴⁰ represents a C₁ to C₈ alkyl group and R⁴¹ represents hydrogen or a C₁ to C₈ alkyl group. Advantageously the total number of carbon atoms in the comonomer

is 5 to 8, and the comonomer is advantageously isoprene. Advantageously, the copolymer contains at least 10% by weight of units derived from butadiene.

(iv) These materials are condensates comprising aromatic and hydrocarbyl parts.

5 The aromatic part is conveniently an aromatic hydrocarbon which may be unsubstituted or substituted with, for example, non-hydrocarbon substituents.

Such aromatic hydrocarbon preferably contains a maximum of three substituent groups and/or three condensed rings, and is preferably naphthalene. The hydrocarbyl part is a hydrogen and carbon containing part connected to the rest of the molecule by a carbon atom. It may be saturated or unsaturated, and straight or branched, and may contain one or more hetero-atoms provided they do not substantially affect the hydrocarbyl nature of the part. Preferably the hydrocarbyl part is an alkyl part, conveniently having more than 8 carbon atoms.

15

In addition, the additive composition may comprise one or more other conventional co-additives known in the art, such as detergents, antioxidants, corrosion inhibitors, dehazers, demulsifiers, metal deactivators, antifoaming agents, cetane improvers, cosolvents, package compatibilities, and lubricity additives and antistatic additives.

20

The co-additives may be added to the additive composition at the same time as any of the additives (I), (II) and if appropriate (III) or at different times.

25

The fuel oil composition, additive composition, or additive concentrate of the fifth to seventh aspects may additionally comprise one or more co-additives useful in fuel oil compositions. Such co-additives include, for example, oxygenates, such as t-butyl methyl ether, antiknock agents, such as methylcyclopentadienyl manganese tricarbonyl, lead scavengers such as aryl or alkyl halides, and detergents, such as alkali or alkaline earth metal salt, polyalkenyl amines, e.g. polybutyleneamines, such as "KEROCOM" polyisobutyleneamine, available ex BASF, Mannich amines, polyalkenyl succinimides, poly(oxyalkylene)amines, poly(oxyalkylene) carbamates, poly(alkenyl)-N-substituted carbamates, and mixtures thereof, and dispersants.

30

Additionally, antioxidants, such as phenolics, e.g. 2,6-di-tert-butylphenol or phenylenediamines, e.g. N,N'-di-sec-butyl-p-phenylenediamine, metal deactivators, demulsifiers and carburetor or fuel injector detergents may be present. Corrosion inhibitors, such as that commercially sold by Rhein Chemie, Mannheim, Germany as "RC 4801", or a polyhydric alcohol ester of a succinic acid derivative having on at least one of its alpha-carbon atoms an unsubstituted or substituted aliphatic hydrocarbon group having from 20 to 500 carbon atoms, for example, pentaerythritol diester of polyisobutylene-substituted succinic acid, the polyisobutylene group having an average molecular weight of about 950, in an amount from about 1 ppmw to about 1000 ppmw, may also be present.

Other Aspects Of the Invention

The invention further provides a process for the manufacture of the fuel oil composition of the first aspect or fourth or fifth aspect, comprising:

- (i) obtaining the desired fuel oil, and
- (ii) blending therewith the additive composition, or additive concentrate, or additives, for example, (I), (II), and optionally (III) of the present invention.

The invention also provides a method of operating an oil refinery or fuel oil manufacturing facility comprising:

- (i) manufacturing a fuel oil with low temperature properties insufficient to meet the required technical specification for that oil,
- (ii) improving such properties through the addition thereto of the additive composition, or additive concentrate, or the additives (I), (II), and optionally (III) of the present invention in an amount sufficient to meet the required specification.

The additive (I) shows excellent physical compatibility with co-additives , for example (II) and (III), and provides enhanced lubricity performance at lower treat rates of additive (I) in combination with additives, for example (II) and (III).

5 An advantage of the invention is that a substantial portion of the aromatic condensate can be replaced by additive (I) in fuel oil compositions which also comprise additive (III) whilst still maintaining or improving the low temperature properties, for example CFPP, and sustaining the wax antissettling performance in fuel oils.

10 Another aspect of the present invention is the use of (I) and (II) and optionally (III) as defined under the first aspect, or the additive composition of the second aspect, or the concentrate of the third aspect, in a fuel oil to improve the lubricity of the fuel oil.

Further the present invention provides the use of (I), (II) and (III) as defined under the
15 first aspect, or the additive composition or additive concentrate of the second and third aspect respectively, each of which comprises, or is obtainable by admixing, (I), (II) and (III) as defined under the first aspect, in a fuel oil to improve the low temperature flow properties of the fuel oil, particularly low temperature filterability.

20 An advantage of the present invention is that additive (I) may be used at reduced treat-rates in fuel oil compositions, which can also contain (II) and optionally (III), particularly in order to enhance lubricity performance.

Another advantage is that additive (I) may be used to replace a substantial portion of
25 aromatic condensate in fuel oil compositions, which also contain (III), whilst maintaining or even improving the low temperature properties, for example CFPP.

In the process, method, use and other aspects of the invention, the preferred
embodiments of (I), (II) and (III) are those as described under the fuel oil composition
30 aspect of the invention.

Further with respect to the fifth to eighth aspects of the present invention, use of additive (I) in combination with a co-additive such as a detergent in a gasoline fuel composition surprisingly results in reduced undesirable effects, for example reduced inlet valve deposits, compared to other lubricity additives.

5

Treat-Rates

Preferably the amount of additive (I) in the fuel oil composition is in the range of from 5 to 500 ppm (active ingredient or a.i) by mass based on the mass of the composition; such as 5 to 250 or 5 to 150; especially 5 to 50; more preferably 10 to 40 ppm by mass; such as 10 to 30 ppm by mass.

10

Preferably the amount of aromatic condensate in the fuel oil composition is not more than 150 ppm (active ingredient or a.i) by mass based on the mass of the composition; more preferably less than 100 ppm by mass; such as less than 75 ppm by mass; especially in the range of from 10 to 50 ppm by mass.

15

Preferably the amount of ethylene polymer in the fuel oil composition is not more than 500 ppm (active ingredient or a.i) by mass based on the mass of the composition; more preferably less than 250 ppm by mass, such as 150 ppm by mass; especially in the range of from 50 to 125 ppm by mass.

20

Preferably the amount of additive (III) in the fuel oil composition is not more than 200 ppm (active ingredient or a.i) by mass based on the mass of the composition; more preferably less than 150 ppm by mass; such as in the range of from 50 to 125 ppm by mass.

25

The effective amount of the combination of (I), (II), and optionally (III) in the fuel oil composition may for example be in the range of 1 to 5,000 ppm (active ingredient) by mass based on the mass of the composition, for example 10 to 5,000 ppm such as 25 to 2500 ppm (active ingredient), preferably 50 to 1000 ppm, more preferably 100 to 800 ppm.

30

Where co-additives are also present, the amount of the additive composition may be correspondingly higher, for example 10 to 10,000 ppm (active ingredient) such as 50 to 5,000 ppm, more preferably 100 to 2,500 ppm.

5

Preferably the ratio of (I):(II):(III) is in the range of from 1 - 50 mass%: 20 - 90 mass %: 0 - 60 mass %; more preferably 2 - 40 mass%: 20 - 80 mass %: 5 - 60 mass %; especially 2 - 30 mass %: 30 - 70 mass %: 10 - 50 mass %.

The invention will now be described further by reference to the examples only as follows:

Examples

- 5 The following materials and procedures were used.

Additive A: 2-hydroxyethyl salicylate

Additive B: mixture of ethylene vinyl acetate growth arrestor and ethylene vinyl acetate nucleator in 3:1 ratio by mass

- 10 Additive C: Nonylphenol-formaldehyde condensate

Additive D: amide – amine salt formed by reacting 1 molar portion of phthalic anhydride with 2 molar proportions of dihydrogenated tallow amine

Fuel oils

	Fuel 1	Fuel 2	Fuel 3	Fuel 4
CFPP Fail temperature	-29°C	-36°C	-9°C	-11°C
Density	0.8215g/l	0.8148g/l	0.8357	0.8302
D86 Distillation (°C)				
IBP	190.2	192.9	173.1	174
D5%	209.3	203.5	198.2	191
D10%	212.9	208.3	201.7	194
D20%	223.0	215.7	215.8	203
D30%	230.2	222.8	227	213
D40%	237.3	231.0	239.1	224
D50%	244.8	238.7	252	237
D60%	252.3	245.9	265.8	254
D70%	260.9	253.5	280.9	272
D80%	271.7	262.3	299.9	295
D90%	285.8	274.8	324.6	323
D95%	297.1	286.1	344.1	342
FBP	307.2	291.2	354.2	354
Flash Point	74.5 °C	73.5 °C		
Pour Point	-24°C	-33°C		
Sulphur content	<100 ppm	<100 ppm		
KV20°C	3.092 cSt	2.996 cSt		
KV40°C	2.035 cSt	2.133 cSt		

15

Fuel oil compositions were prepared in the proportions shown in the Examples and the resulting fuel oil compositions were tested in the High Frequency Reciprocating Rig Test (or "HFRR") for lubricity performance. The HFRR test method is described

in the industry standard test methods CEC PF 06-T-94 and ISO/TC22/SC7/WG6/W188 and was performed at 60°C. Selected fuel oil compositions were also tested to evaluate their ability to improve the low temperature properties of a fuel, as measured by their CFPPs, as described in European Standard method EN116.

Comparative Example 1

Fuel oil compositions were prepared in the proportions shown below in Fuel 1 and tested in the HFRR.

Treat rate (ppm ai)					HFRR (μ)
Additive A	Additive B	Additive C	Additive D	Total	
0	-	-	-	0	656
25	-	-	-	25	538
50	-	-	-	50	543
75	-	-	-	75	533
100	-	-	-	100	426
150	-	-	-	150	400
200	-	-	-	200	337
-	150	-	-	150	636
-	200	-	-	200	626
-	-	150	-	150	644
-	-	200	-	200	574
-	-	62.5	62.5	125	602
-	-	75	75	150	535
-	-	100	100	200	411

Example 1

Fuel oil compositions were prepared in the proportions shown below in Fuel 1 and tested in the HFRR.

Treat rate (ppm ai)			HFRR (μ)
Additive A	Additive B	Total	
37.5	112.5	150	577
50	150	200	317

The data clearly show that the HFRR performance is improved as the total treat rate of Additive A and Additive B is increased from 150 to 200ppm. Further, the Applicant

was surprised to find that good HFRR performance is achieved at treat rates as low as 50 ppm of Additive A in combination with Additive B (see Comparative Example 1).

5 Example 2

Fuel oil compositions were prepared in the proportions shown below in Fuel 1 and tested in the HFRR.

Treat rate (ppm ai)				HFRR (μ)
Additive A	Additive C	Additive D	Total	
38	113	-	150	369
50	150	-	200	303
19	56	75	150	350
25	75	100	200	313
30	45	45	120	313

Similar to Example 1, the data clearly show an improvement in the HFRR performance for compositions containing both Additive A and C, in particular at low treat rates of Additive A (see Comparative Example 1). This trend is also observed for compositions containing Additive A, C and D.

15 Example 3

Fuel oil compositions were prepared in the proportions shown below in Fuel 1 and tested in the HFRR.

Treat rate (ppm ai)					HFRR (μ) ¹
Additive A	Additive B	Additive C	Additive D	Total	
16	100	47	63	225	266
-	100	47	63	210	585
-	100	63	63	226	466
20	-	94	-	114	534
20	100	94	-	214	384

¹average of 3 measurements

Compositions containing Additives A, B, and C demonstrated enhanced HFRR performance compared to compositions containing only Additives A and C. This is particularly significant at lower treat rates of Additive A (see Example 2).

Example 4

Fuel oil compositions were prepared in the proportions shown below in Fuel 3 and tested in the HFRR and their CFPP measured. Each composition also contained Additive B at 100 ppm (active ingredient) for CFPP measurements.

5

Treat rate (ppm ai)			CFPP (°C)	HFRR (μ)
Additive A	Additive C	Additive D		
-	-	100	-27	-
-	50	50	-27	455
20	35	45	-28	245

Example 5

Fuel oil compositions were prepared in the proportions shown below in Fuel 4 and tested in the HFRR and their CFPP measured. Each composition also contained an ethylene vinyl acetate growth arrestor (28 wt % vinyl acetate and 72 wt % ethylene; having a number average molecular weight of 3200) at 100 ppm (active ingredient) for CFPP measurements.

10

Treat rate (ppm ai)			CFPP (°C)	HFRR (u)
Additive A	Additive C	Additive D		
-	-	100	-25	-
-	50	50	-21	562
20	35	45	-27	280

15 The data in Examples 4 and 5 clearly show an improvement in the HFRR performance at low treat rates of Additive A whilst maintaining, or even improving, the CFPP performance.

20

Example 6

Fuel oils

	Fuel 5	Fuel 6
Density @ 15°C (g/L)	0.7393	0.7491
RON (research octane number)	96.8	95.5
MON (motor octane number)	85	84.8
Distillation		
IBP	26.9	29.5
10%	43.3	48
20%	51.4	59.5
30%	60.3	71.5
40%	71.2	84.5
50%	84.5	97.5
60%	102.1	110.5
70%	119.1	124.0
80%	130.8	139.0
90%	150.7	158.0
95%	168.2	170.0
FBP	199.7	196.5
Sulfur (mass %)	0.013	0.0165

5 Additives

Additive E: a PIB amine detergent (1300 Mw PIB)

Additive F: a PIB amine detergent (950 Mw PIB)

Additive G: glycerol mono- and di-esters of unsaturated fatty acids (a lubricity additive)

10 Additive H: ethoxylated C36 dimer acid (a lubricity additive)

Gasoline fuel oil compositions were prepared in the proportions shown below and the resulting fuel oil compositions were tested in Mercedes-Benz M102 E test according to procedure CEC F-05-A-93.

	Additive Treat rate (ppm ai)					fuel
	E	F	A	G	H	
Example 6a (comparative)	480	-	-	-	-	5
Example 6b (comparative)	480		-	100	-	5
Example 6c (comparative)	480	-	-	-	100	5
Example 6d (comparative)^	-	-	-	-	-	6
Example 6e (comparative)	-	581	-	-	-	6
Example 6f (comparative)	-	670	-	-	-	6
Example 6	-	670	100	-	-	6

5 ^Example 6d is base fuel

Briefly, the M102E test evaluates the effect of gasoline fuel compositions on the formation of inlet valve deposits, in passenger car engines with fuel injection. This test allows the effectiveness of different fuel additives to be evaluated.

5

Results of M102E Test

	Inlet Valve Desposits (mg/valve)					CCD* (g/cylinder)	Valve rating
	V1	V2	V3	V4	Ave.	Ave.	Ave.
Example 6a	49	61	167	185	116	1.9313	9.1
Example 6b	597	617	591	728	633	1.739	7.2
Example 6c	845	1200	1194	1340	1145	1.919	6.1
Example 6d	340	232	354	388	329	1.520	7.8
Example 6e	44	58	125	53	70	2.134	9.4
Example 6f	27	48	9	4	22	2.235	9.8
Example 6	34	246	47	101	107	1.987	9.1

* combustion chamber deposits

The results show that when a detergent additive is present, then good performance is observed (see Examples 6a & 6d to 6f). However, on addition of certain lubricity additives, for example additives G and H to the fuel composition, which also has a detergent, the inlet valve deposits are substantially increased (see Examples 6a-6c).

In contrast and surprisingly, the use of additive A, an example of additive (I) according to the invention, results in minimising the increase in inlet valve deposits (see Example 6 compared to Examples 6d to 6f).

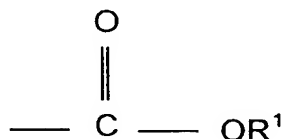
CLAIMS

1. A fuel oil composition comprising, or obtainable by admixing, a major amount of a fuel oil and minor amounts of:

(I) one or more compounds having at least one aromatic ring system, wherein at least one ring system bears, as substituents,

(a) one or more hydroxyl groups or derivatives thereof or both; and

(b) one or more ester groups of the formula



where R^1 represents a hydrocarbyl group having at least one hydroxyl group or a derivative thereof or both;

(II) one or more aromatic condensates other than those defined in (I) or one or more ethylene polymers or both; and

(III) optionally, one or more oil-soluble polar nitrogen compounds.

2. An additive composition comprising, or obtainable by admixing, (I), (II) and optionally (III) as defined in claim 1.

3. An additive concentrate comprising, or obtainable by admixing, either (I), (II) and optionally (III) as defined in claim 1 or the additive composition of claim 2, and a compatible solvent therefor.

4. The fuel oil composition of claim 1, obtainable by admixing a fuel oil and either the additive composition of claim 2 or the additive concentrate of claim 3.

5. The composition or concentrate of any one of the preceding claims wherein the aromatic ring system of the compound (I) is a single, six-membered ring.

5 6. The composition or concentrate of claim 5 wherein the compound (I) comprises a single benzene ring bearing

(i) one hydroxyl group (a), and

(ii) one ester group (b).

10 7. The composition or concentrate of any one of the preceding claims wherein R¹ represents a hydroxyl-substituted alkyl substituent.

15 8. The composition or concentrate of any of the preceding claims wherein at least one aromatic condensate is present and is preferably a condensate of formaldehyde and phenol or a substituted phenol.

20 9. The composition or concentrate of any of the preceding claims wherein at least one ethylene polymer is present and is preferably an ethylene unsaturated ester copolymer.

25 10. The composition or concentrate of any of the preceding claims wherein at least one compound (III) is present and wherein the or each such compound is a nitrogen compound carrying one or more substituents of the formula $>NR^{13}$, wherein R¹³ represents a hydrocarbyl group containing 8 to 40 carbon atoms, optionally in the form of a salt thereof.

30 11. A fuel oil composition comprising, or obtainable by admixing, a major amount of hydrocarbons boiling in the gasoline range and minor amounts of (I) as defined in any one of claims 1, 5, 6 or 7, and optionally and one or more gasoline co-additives selected from anti-knock agents, lead scavengers, detergents,

dispersants, antioxidants, metal deactivators and carburetor or fuel injector detergents.

- 5 12. An additive composition comprising, or obtainable by admixing, (I) as defined in any one of claims 1, 5, 6 or 7, and optionally one or more gasoline co-additives selected from anti-knock agents, lead scavengers, detergents, dispersants, antioxidants, metal deactivators and carburetor or fuel injector detergents.
- 10 13. A concentrate comprising, or obtainable by admixing, either the additive composition claimed in claim 12 or (I) as defined in any one of claims 1, 5, 6 or 7, and one or more gasoline co-additives selected from anti-knock agents, lead scavengers, detergents, dispersants, antioxidants, metal deactivators and carburetor or fuel injector detergents, and a compatible solvent therefor.
- 15 14. The use of (I) as defined in any one of claims 1, 5, 6 or 7 and optionally one or more gasoline co-additives selected from anti-knock agents, lead scavengers, detergents, dispersants, antioxidants, metal deactivators and carburetor or fuel injector detergents for improving the friction of a fuel composition comprising a major amount of hydrocarbons boiling in the gasoline range

THIS PAGE IS BLANK (ISPTO)

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
25 October 2001 (25.10.2001)

PCT

(10) International Publication Number
WO 01/79397 A3

- (51) International Patent Classification⁷: **C10L 1/14**
10/04, 10/00
- (21) International Application Number: **PCT/EP01/04177**
- (22) International Filing Date: **11 April 2001 (11.04.2001)**
- (25) Filing Language: **English**
- (26) Publication Language: **English**
- (30) Priority Data:
0009310.4 **17 April 2000 (17.04.2000)** **GB**
- (71) Applicant (*for all designated States except US*): **INFINEUM INTERNATIONAL LTD.** [GB/GB]; P.O. Box 1, Law Department, Milton Hill, Abingdon, Oxon, Oxfordshire OX13 6BB (GB).
- (72) Inventors; and
- (75) Inventors/Applicants (*for US only*): **JACKSON, Graham** [GB/GB]; 270A Kidmore Road, Caversham, Reading, Berkshire, Berkshire RG4 7NE (GB). **FAVA, Carlo** [IT/GB]; 7B Blandford Avenue, Oxford, Oxfordshire OX2 8EA (GB).
- (74) Agent: **HART, Richard, Joseph**; Infineum UK Limited, Law Department, PO Box 1, Milton Hill, Abingdon, Oxon, Oxfordshire OX13 6BB (GB).
- (81) Designated States (*national*): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CR, CU, CZ, DE, DK, DM, DZ, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW.
- (84) Designated States (*regional*): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).
- Published:**
— *with international search report*
- (88) Date of publication of the international search report:
7 March 2002
- For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.*



WO 01/79397 A3

(54) Title: **FUEL OIL COMPOSITIONS**

(57) Abstract: **Oils having improved lubricity and low temperature properties and additives for use therein.**

INTERNATIONAL SEARCH REPORT

Inte. onal Application No

PCT/EP 01/04177

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C10L1/14 C10L10/04 C10L10/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C10L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P, X	WO 00 27953 A (SHELL INT RESEARCH) 18 May 2000 (2000-05-18) page 7, line 2 page 8, line 17	1-9
Y	WO 98 16596 A (DEORE CHRISTOPHE LE ;CAPROTTI RINALDO (GB); EXXON CHEMICAL PATENTS) 23 April 1998 (1998-04-23) cited in the application page 17, line 35	1-7, 9, 10
Y	WO 96 18708 A (DILWORTH BRID ;CAPROTTI RINALDO (GB); DAVIES BRIAN WILLIAM (GB); E) 20 June 1996 (1996-06-20) the whole document	1-7, 9, 10

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

- *T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- *G* document member of the same patent family

Date of the actual completion of the international search

4 October 2001

Date of mailing of the international search report

12/10/2001

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

De La Morinerie, B

INTERNATIONAL SEARCH REPORT

Inte. lional Application No

PCT/EP 01/04177

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4 098 708 A (STUEBE CARL WALTER) 4 July 1978 (1978-07-04) column 10, line 30 -column 11, line 8 ----	11-13
X	WO 94 14926 A (CHEVRON RES & TECH) 7 July 1994 (1994-07-07) page 25 ----	11-13
A	WO 99 61562 A (INFINEUM UK LTD ;INFINEUM USA LP (US)) 2 December 1999 (1999-12-02) cited in the application the whole document ----	1-14
A	WO 96 18706 A (DILWORTH BRID ;CAPROTTI RINALDO (GB); DAVIES BRIAN WILLIAM (GB); E) 20 June 1996 (1996-06-20) the whole document ----	1-4,10
A	EP 0 704 425 A (IDEMITSU KOSAN CO) 3 April 1996 (1996-04-03) page 27, line 32 - line 39 -----	1,11-14

INTERNATIONAL SEARCH REPORT

Information on patent family members

Int. Application No

PCT/EP 01/04177

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
WO 0027953	A	18-05-2000	AU WO 1388000 A 0027953 A1	29-05-2000 18-05-2000
WO 9816596	A	23-04-1998	AU 735566 B2 AU 4555197 A CN 1237995 A WO 9816596 A1 EP 0931124 A1 FI 990793 A JP 2001505935 T NO 991713 A US 6258135 B1	12-07-2001 11-05-1998 08-12-1999 23-04-1998 28-07-1999 01-06-1999 08-05-2001 11-06-1999 10-07-2001
WO 9618708	A	20-06-1996	CA 2182993 A1 CA 2182995 A1 CA 2183180 A1 DE 69517514 D1 DE 69517514 T2 DE 69518404 D1 DE 69518404 T2 WO 9618706 A1 WO 9618707 A1 WO 9618708 A1 EP 1028155 A1 EP 1050573 A2 EP 0743973 A1 EP 0743974 A1 EP 0743972 A1 JP 9509450 T JP 9509451 T JP 9509452 T US 5858028 A US 6010545 A US 5833722 A AT 176274 T AU 704905 B2 AU 6699596 A BR 9609767 A CA 2223653 A1 DE 69601472 D1 DE 69601472 T2 DK 839174 T3 WO 9704044 A1 EP 0839174 A1 ES 2127022 T3 FI 980047 A JP 11509255 T NO 980143 A US 5882364 A ZA 9606013 A	20-06-1996 20-06-1996 20-06-1996 20-07-2000 02-11-2000 21-09-2000 25-01-2001 20-06-1996 20-06-1996 20-06-1996 16-08-2000 08-11-2000 27-11-1996 27-11-1996 27-11-1996 22-09-1997 22-09-1997 22-09-1997 12-01-1999 04-01-2000 10-11-1998 15-02-1999 06-05-1999 18-02-1997 26-01-1999 06-02-1997 11-03-1999 16-09-1999 13-09-1999 06-02-1997 06-05-1998 01-04-1999 13-01-1998 17-08-1999 06-03-1998 16-03-1999 31-01-1997
US 4098708	A	04-07-1978	NONE	
WO 9414926	A	07-07-1994	US 5427591 A AT 193313 T AU 671187 B2 AU 5852294 A BR 9305914 A	27-06-1995 15-06-2000 15-08-1996 19-07-1994 19-08-1997

INTERNATIONAL SEARCH REPORT

Information on patent family members

Int. Application No

PCT/EP 01/04177

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
WO 9414926	A		CA 2130187 A1 DE 69328721 D1 DE 69328721 T2 EP 0636164 A1 JP 7506119 T WO 9414926 A1	07-07-1994 29-06-2000 28-12-2000 01-02-1995 06-07-1995 07-07-1994
WO 9961562	A	02-12-1999	AU 4143199 A WO 9961562 A1 EP 1088045 A1 US 6232277 B1	13-12-1999 02-12-1999 04-04-2001 15-05-2001
WO 9618706	A	20-06-1996	CA 2182993 A1 CA 2182995 A1 CA 2183180 A1 DE 69517514 D1 DE 69517514 T2 DE 69518404 D1 DE 69518404 T2 WO 9618706 A1 WO 9618707 A1 WO 9618708 A1 EP 1028155 A1 EP 1050573 A2 EP 0743973 A1 EP 0743974 A1 EP 0743972 A1 JP 9509450 T JP 9509451 T JP 9509452 T US 5858028 A US 6010545 A US 5833722 A AT 176274 T AU 704905 B2 AU 6699596 A BR 9609767 A CA 2223653 A1 DE 69601472 D1 DE 69601472 T2 DK 839174 T3 WO 9704044 A1 EP 0839174 A1 ES 2127022 T3 FI 980047 A JP 11509255 T NO 980143 A US 5882364 A ZA 9606013 A	20-06-1996 20-06-1996 20-06-1996 20-07-2000 02-11-2000 21-09-2000 25-01-2001 20-06-1996 20-06-1996 20-06-1996 16-08-2000 08-11-2000 27-11-1996 27-11-1996 27-11-1996 22-09-1997 22-09-1997 22-09-1997 12-01-1999 04-01-2000 10-11-1998 15-02-1999 06-05-1999 18-02-1997 26-01-1999 06-02-1997 11-03-1999 16-09-1999 13-09-1999 06-02-1997 06-05-1998 01-04-1999 13-01-1998 17-08-1999 06-03-1998 16-03-1999 31-01-1997
EP 0704425	A	03-04-1996	JP 7267904 A AU 679076 B2 AU 6936594 A EP 0704425 A1 JP 7331263 A US 5686398 A CA 2163657 A1 WO 9429264 A1	17-10-1995 19-06-1997 03-01-1995 03-04-1996 19-12-1995 11-11-1997 22-12-1994 22-12-1994

INTERNATIONAL SEARCH REPORT

Information on patent family members

Int. l. Application No

PCT/EP 01/04177

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 0704425	A	JP 7062371 A JP 7165671 A	07-03-1995 27-06-1995